Thermochimica Acta 657 (2017) 20–25

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Full Length Article

Thermochemistry of hydrogen bonding of proton acceptors in the media of linear and cyclic amides. Cooperativity effects in multi-particle complexes of amides

Ilnaz T. Rakipov*, Artem A. Petrov, Aydar A. Akhmadiyarov, Artashes A. Khachatrian, Mikhail A. Varfolomeev, Boris N. Solomonov

Department of Physical Chemistry, Kazan Federal University, Kremlevskaya 18, Kazan, 420008, Russia

ARTICLE INFO

Keywords:
Solution enthalpies
Linear and cyclic amides
Proton acceptors
Hydrogen bonding
Solution calorimetry
Cooperativity effect

ABSTRACT

In present work a thermochemistry of hydrogen bond formation of proton acceptors (B) in the medium of linear (*N*-methylformamide (NMF)) and cyclic (2-pyrrolidone (Py)) amides was studied. The infinite dilution solution enthalpies of nitriles, ketones, esters, ethers and amines in amides were measured at 298.15 K. Enthalpies of hydrogen bonding of proton acceptors in solution linear and cyclic amides were calculated and compared with previously determined the enthalpies of hydrogen bonding of amides in proton acceptor media. The cooperative effects of hydrogen bonding in multi-particle complexes of amides with proton acceptors were evaluated. It was shown that cooperativity coefficients were decreased with increasing the basicity of proton acceptors.

1. Introduction

Amides are the closest model compounds to study the hydrogen bonds in proteins and peptides [1–4]. Moreover, linear and cyclic amides themselves have wide practical applications as solvents for the separation processes [5], as electrolytes for lithium-ion batteries [6–8], and as ligands for catalytic reactions [9]. Also, amides are used as components of anticancer drugs [10,11]. Physical-chemical properties of amides in all above-mentioned systems are realized through different types of intermolecular interactions (including hydrogen bonding).

The hydrogen bond formation of amides with organic molecules was studied by different experimental methods: IR-spectroscopy [1,3,12], UV-spectroscopy [2,3], NMR-spectroscopy [13,14], solution calorimetry [15–18] and computational chemistry [2,3,19–21]. Authors of these works analyzed hydrogen bonds strengths of amides with different proton donors and proton acceptors and also investigated acid-base properties of amides during interaction with aliphatic alcohols. Kimura et al.[17] found that linear and cyclic aprotic amides have equal proton acceptor ability. However, these compounds can be able to exhibit various proton-donor properties in solution [22].

Primary and secondary amides can form self-associative species due to N–H…O=C hydrogen bonds between different molecules. Self-association significantly affects the properties of primary and secondary amides in comparison with tertiary amides which do not have this possibility. Self-association of amides was studied in several works, for example [23–25]. It was shown that such phenomenon as cooperativity of hydrogen bonds occurs in amide solutions [23,24]. Cooperativity effect changes the acid-base properties of the molecules. In works [13,14] it was shown that increase of length of alkyl substituents in the molecules of acetamides significantly to decreases the value of self-aassociation enthalpy. It was noted that enthalpies of association of amides in tetrachloromethane are higher than in 1,4-dioxane due to breaking of amide–amide hydrogen bonds. Cooperative effects manifest themselves in multi-particle complexes A…$(HX)_n$ which could be formed during interaction of molecule (A) with the self-associated solvent species $(HX)_n$ [26–33].

Cooperativity of hydrogen bonds determines the structure and properties of self-associated solvents (water, alcohols, amides, etc.) [27,29,34–37]. Cooperative effects define molecular recognition [38,39], play key role in the synthesis and stability of supramolecular systems [40,41], and biomolecules like peptides and proteins [42–44]. The hydrogen bond in the ternary systems RN…H(R)O…HOR was shown to be enhanced by up to 20–30% compared with the double complexes ROH…NR [29]. The cooperative effect was noted to be weakly dependent on the length and branching of the alkyl radical of alcohol molecule [29,30,33]. Cooperative effects (strengthening) or anti-cooperative effects (weakening) of hydrogen bonds were shown to be able to manifest themselves in multi-particle complexes due to the formation of clusters of different composition [45–48]. The manifestation of cooperative effects of hydrogen bonds in three-particle systems

* Corresponding author.
E-mail address: ilnaz0805@gmail.com (I.T. Rakipov).

http://dx.doi.org/10.1016/j.tca.2017.09.012
Received 23 May 2017; Received in revised form 5 September 2017; Accepted 9 September 2017
Available online 12 September 2017